

STABILITY RESULTS OF A  
CONTINUOUS STIRRED TANK REACTOR

By

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## NOTATION

$A$	heat transfer area between reactor and coolant
$B$	dimensionless heat of reaction parameter
$C$	conversion in reactor
$C_{in}$	reactant concentration at inlet
$C_p, C_{pc}$	specific heats of reactant and coolant respectively
$C^{ss}$	steady-state conversion
$D$	determinant of matrix $M$
$Da$	Damkohler number, dimensionless parameter
$E$	activation energy of reaction
$(-\Delta H)$	heat of reaction
$k_0$	reaction rate constant evaluated at $T_{in}$
$k_T$	thermal conductivity
$l$	length of cooling coil or catalytic wire
$Le$	dimensionless number, similar to Lewis number, defined in equation 2.3
$M$	Jacobian matrix in equation 3.1
$n$	degree of characteristic equation
$P$	sum of principal $2 \times 2$ minors of $M$
$q, q_c$	flow rates of reactant and coolant respectively
$R$	universal gas constant
$s$	characteristic equation variable, eigenvalue
$S$	perimeter of cooling coil

$T$	dimensionless reactant temperature
$T_C$	dimensionless coolant temperature
$T_{cin}$	dimensionless inlet coolant temperature
$T_{in}$	inlet reactant temperature
$T^{ss}, T_C^{ss}$	steady-state values of reactant and coolant temperatures
$U$	overall heat transfer coefficient
$V, V_C$	volume of reactor, cooling jacket respectively
$v_C$	velocity of coolant
$w$	imaginary part of $s$
$x$	variable defined in equation 3.1
$z$	steady-state conversion, equals $C^{ss}$

#### Greek

$\alpha_2$	dimensionless parameter
$\beta_M$	modified heat transfer coefficient
$\beta_P$	dimensionless heat transfer coefficient, identical with Poore's definition
$\delta$	discriminant of the cubic characteristic equation
$\eta$	parameter in characteristic equation
$\xi$	parameter in characteristic equation
$\rho, \rho_C$	densities of reactant, coolant respectively
$\sigma$	real part of eigenvalue $s$
$\Delta$	determinant defined in equation 4.6

### Subscripts

c	coolant variable
in	variable at inlet
g	gas phase temperature for the reaction on a wire

### Superscripts

'	deviation variable
*	amplitude of deviation variable
~	dimensional variables
ss	steady-state variable
w	catalytic wire variable

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Instabilities of many different kinds occur in chemical reactor systems. These are primarily due to the nonlinear effects in the processes occurring in these systems. The simplest of the systems which give rise to the interesting phenomena as limit cycles, multiple steady states are the first order reaction in a continuous stirred tank reactor (CSTR). The strong nonlinear dependence of the reaction rate on temperature gives rise to these phenomena. In order to achieve tractability of the problem, it is common practice to make assumptions. These simplify the equations and yet retain the essential features of the system.

This dissertation can be divided into two parts. In the first part, we modify the equations governing a CSTR by considering the finite thermal capacity of the cooling jacket. This relaxes the assumption that the coolant temperature is a constant at its inlet value. The energy balance equation for the coolant is considered and we study its influence on the stability of the steady-states.



In the latter part, a completely new and different approach to the CSTR problem is discussed. The standard method of analysis for the CSTR is to fix the parameters and then evaluate the steady-state conversion and its stability. The limitation of this method is we do not know the conversion and its stability until we finish solving the problem. The new method involves calculating the entire combination of parameter values which yield an asymptotically stable conversion level. The D-partition method is used to accomplish this.

In the conclusions section, the evolution of the dissertation in its final form is discussed. Promising avenues for future work are described, i.e., studying chaotic dynamics, quasiperiodic oscillations. These should be feasible extensions of the model we have studied.

## CHAPTER 1 INTRODUCTION

The exothermic first order reaction



in a continuous stirred tank reactor (CSTR) has been studied extensively in the chemical engineering literature (Poore, 1973). In a typical reactor (Figure 1.1) the reactant A enters the reactor at a fixed concentration and temperature. Under the conditions of perfect mixing the effluent concentration and temperature are the same as those existing inside the reactor. In a non-adiabatic reactor a coolant fluid is usually circulated through a cooling coil/jacket encasing the reactor. The coolant absorbs a part of the heat released by the exothermic reaction preventing the temperature from increasing in an uncontrolled manner.

The strong nonlinear dependence of the reaction rate on temperature gives rise to many interesting dynamic behaviors. The first elaborate treatment of this problem was given by Poore (1973). He studied the dynamics of the system, obtaining conditions for occurrence of multiple steady states, hysteresis loops and limit cycles. His model contains three dimensionless parameters. He classified his 3-parameter space into different regions, each region having its own characteristic behavior of solutions. The algebraic tractability of this problem has made

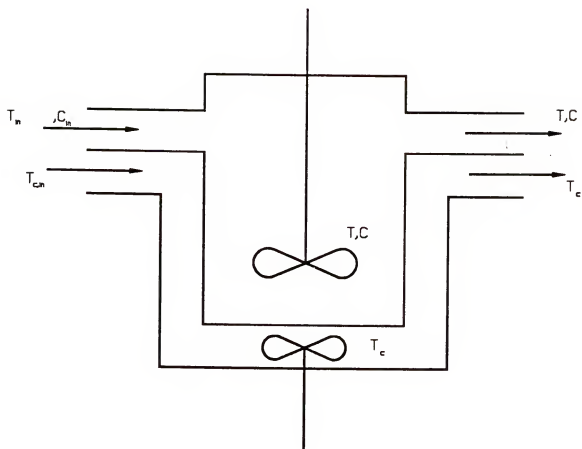


Figure 1.1. A typical continuous stirred tank reactor

it a worthwhile effort for many investigators to study this problem. Most studies since then have focused on (a) studying the effects of different kinetics, typically considering Arrhenius kinetics with a finite activation energy; (b) using a different parameter, i.e., flow rate as a control variable. The works of Uppal et al. (1974, 1976) and Balakotaiah et al. (1981) come to mind.

All analyses of the non-adiabatic reactor have so far neglected the rise in temperature of the coolant fluid. This assumption of a constant or negligible change of the coolant temperature is valid in the limit of infinitely fast flow of the cooling fluid or in the limit of infinite volume of the cooling coil/jacket. In the former case, the coolant does not spend enough time in the jacket to gain enough heat to register a significant change in its temperature. Here the constant coolant temperature is equal to its inlet value. In the latter case, the thermal inertia of the cooling jacket is very high. Hence, here once again although the coolant absorbs heat from the reactor, its temperature change is negligible since the jacket acts as an infinite sink. Now the coolant temperature remains constant at its initial value.

In the first part of this dissertation, the dynamics of a CSTR supporting a first order reaction are modelled by taking into account the effect of the heat absorbed by the coolant fluid, i.e., considering a finite volume of the cooling jacket/coil and a finite rate of the flow of the coolant. Under these conditions, the assumption of constant coolant temperature breaks down. In reality the coolant temperature varies along the coil. However as a first approximation (see Appendix A), a simplistic model would be to study the dynamics of the coolant by assuming it to be well mixed and doing an overall heat balance on the

coolant fluid. This enables us to neglect spatial variations in the equation for the coolant fluid. We then have an overall lumped parameter model for our system.

A brief discussion of the remaining sections now follows. In the next section of the dissertation, the mathematical model of our system and the calculation of its steady-state behavior are discussed. As a first step towards looking for any dynamical behavior, a linear stability analysis was then performed to obtain conditions for the onset of limit cycles. This gives us some insight into the dynamic behavior of our model. We study the stability and bifurcation of the steady-state in terms of our parameters. The main objective of this part is to investigate how inclusion of the finite thermal capacity of the coolant alters the stability of steady-states. The focus is on finding whether existing unstable steady-states can be stabilized by changing the coolant residence time.

In the second part of the dissertation, a different approach to solving the CSTR problem is described. The standard method used in the literature so far has been to study the stability of the steady state conversion for a fixed combination of parameter values. We try to answer the question--What are the total possible combinations of parameters which yield an asymptotically stable steady conversion level? This is done using the D-partition method. Its applications to the standard CSTR (Poore, 1973) model and our model is discussed. The usefulness of this method over the standard method is explained. In the conclusions section, possible avenues for future research are discussed. These should be feasible extensions of the model presented here.

## CHAPTER 2 MODEL AND STEADY-STATE BEHAVIOR

The equations modelling the standard non-adiabatic CSTR (i.e., with coolant temperature assumed to be a constant) following Poore (1973) are

$$\frac{dC}{dt} = -C + Da(1-C)e^T \quad (2.1)$$

$$\frac{dT}{dt} = -T + BDa(1-C)e^T - \beta_p(T-T_c) \quad (2.2)$$

where

$$C = 1 - C_A/C_{in} \quad T = \frac{E}{RT_{in}^2} (\bar{T} - T_{in}) \quad B = \frac{(-\Delta H)C_{in}E}{RT_{in}^2 \rho C_p}$$

$$Da = \frac{Vk_o}{q} \quad \beta_p = \frac{UA}{q\rho C_p}$$

Here the dependent variables  $C$ ,  $T$  represent dimensionless conversion and temperature. The parameters  $(-\Delta H)$ ,  $k_o$ ,  $E$ ,  $T_{in}$ ,  $C_A$ ,  $C_{in}$ ,  $R$ ,  $q$ ,  $C_p$ ,  $\rho$ ,  $V$ ,  $U$ ,  $A$  represent heat of reaction, rate constant of reaction, activation energy, inlet temperature of reactants, reaction concentration, inlet concentration of reactant, universal gas constant, reactant flow rate, reactant specific heat, reactant density, volume of reactor, overall heat transfer coefficient, and surface area for heat exchange respectively. Here we have made the exponential approximation (Aris, 1975) in an attempt to simplify the Arrhenius kinetics. Here '-' denotes dimensioned variables.  $T_c$  is the assumed constant dimensionless coolant temperature scaled as  $T$ . If we neglect this assumption and take

the coolant to be perfectly mixed, i.e., neglect spatial gradients, the energy balance for the coolant becomes

$$Le \frac{dT_c}{dt} = \alpha_2 (T_{cin} - T_c) + (T - T_c) \quad (2.3)$$

where

$$Le = \frac{V_c \rho_c C_{pc} q}{UAV}, \quad \alpha_2 = \frac{q_c \rho_c C_{pc}}{UA}, \quad T_c = \frac{E (\bar{T}_c - T_{in})}{RT_{in}^2},$$

$$T_{cin} = \frac{E (\tilde{T}_{cin} - T_{in})}{RT_{in}^2}$$

The derivation of these equations is shown in Appendix A. A similar energy balance for the cooling jacket was done by Mukesh and Cooper (1986). They simulate the CSTR using the outlet coolant temperature as a variable to control the reactor. Consequently they are forced to study the reactor dynamics by including the energy balance for the coolant. They study the effect of sampling time on the onset of limit cycles in their reactor.

In (2.3)  $T_c$  is the outlet coolant temperature which is the same as the coolant temperature in the jacket. However, this differs from the inlet coolant temperature  $T_{cin}$  (see Appendix A). We have introduced two new dimensionless parameters  $Le$  and  $\alpha_2$ . The parameter  $Le$  is not the same as the traditional Lewis number. It is similar to it for two reasons. First, it multiplies the time derivative term as the standard Lewis number. Secondly, it can be looked upon as a ratio of two time scales. The parameters having a subscript 'c' represent the coolant variable analogs of the corresponding reactor variables. The equations modelling the CSTR now become (2.1-2.3).

The choice of the dimensionless groups is such that we have a very close parallel to Poore's model. The parameters  $B$ ,  $Da$ ,  $\beta_p$  in (2.1,2.2) are similar to the parameters  $B$ ,  $Da$ ,  $\beta$  of Poore's model. This facilitates comparison of our results with Poore's results under certain limiting conditions as  $Le \rightarrow 0$ ,  $Le \rightarrow \infty$ .

The advantages in choosing the dimensionless groups  $Le$ ,  $\alpha_2$  in equation (2.3) are as follows:

1. The parameter  $Le$  multiplies the time derivative term in (2.3). Hence, the steady-state solution obtained by setting the time derivative to zero is independent of  $Le$ . This facilitates computations as we will explain later.
2. The parameter  $q_c$  the coolant flow rate occurs in only one dimensionless parameter  $\alpha_2$ . Hence,  $\alpha_2$  can be used as a control parameter.
3. In the limits of  $Le \rightarrow 0$ ,  $Le \rightarrow \infty$ , the results offer easy comparison with Poore's results. Besides in these limits it may be possible to apply singular perturbation methods and seek the existence of relaxation oscillations. Our system may also exhibit quasi-periodic oscillations.

The steady-state solutions are given by

$$0 = -C^{ss} + Da(1-C^{ss})e^{\frac{BC^{ss} + \beta_M T_{cin}^{ss}}{1 + \beta_M}} \quad (2.4)$$

$$T^{ss} = (BC^{ss} + \beta_M T_{cin}^{ss}) / (1 + \beta_M) \quad (2.5)$$

$$T_c^{ss} = (T^{ss} + \alpha_2 T_{cin}^{ss}) / (1 + \alpha_2) \quad (2.6)$$



Here superscript 'ss' denotes a steady state solution.

$\beta_M = \frac{\beta_p \alpha_2}{1 + \alpha_2}$  is a modified or effective heat transfer coefficient. The steady state solution, thus, depends only on  $Da$ ,  $B$ ,  $\beta_M$ . It is independent of  $Le$  and depends on  $\beta_p$ ,  $\alpha_2$  through  $\beta_M$ . Equation (2.4) is identical with Poore's equation for steady-state conversion with his  $\beta$ ,  $T_c$  playing the role of our  $\beta_M$ ,  $T_{cin}$ . We can thus use Poore's results to map his steady curves to our curves realizing the analogy between our  $\beta_M$  and Poore's  $\beta$ .

The nonlinear equation (2.4) can have multiple solutions for some combinations of  $B$ ,  $Da$ ,  $\beta_M$ . Following Poore, we require for unique solutions  $\frac{dDa}{dC} \geq 0$ . Thus a necessary and sufficient condition for unique solutions is  $B \leq 4(1 + \beta_M)$ . For  $B > 4(1 + \beta_M)$  there exists a range of  $Da$  for which equation (2.4) has three solutions. Figures 2.1 and 2.2 are plots of steady-state conversion versus  $Da$  for the two cases of unique solutions for all  $Da$  and multiple solutions for some values of  $Da$  respectively. Typical order of magnitude estimates for the various dimensionless parameters are given in Table 1. These estimates have been obtained from the values of parameters quoted in experimental studies in the literature (see Appendix B). All computations and diagrams are based on values of parameters taken from these ranges.

Hence, the behavior of the steady states is very similar to the standard Poore problem. This facilitates the study of the role of the parameter  $Le$  on the onset of limit cycles.

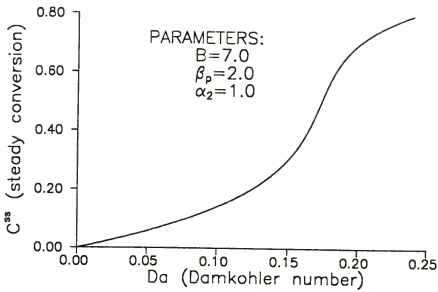


Figure 2.1. Unique steady states

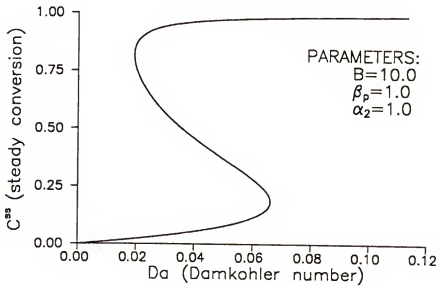


Figure 2.2. Multiple steady states

TABLE 1

Order of Magnitude Estimates of Dimensionless Parameters

Parameter	Order of Magnitude
B	$10^0 - 10^1$
Da	$10^{-2} - 10^{-1}$
Le	$10^{-1} - 10^0$
$\alpha_2$	$10^{-1} - 10^0$
$\beta_p$	$10^{-1} - 10^0$

### CHAPTER 3 LINEAR STABILITY ANALYSIS

In the previous chapter, the calculation and characterization of the steady-state solutions of our CSTR were described. The stability of these steady states to infinitesimal perturbations is now discussed using a linear stability analysis.

Linearizing the equations (2.1-3) about the steady-state solutions we obtain

$$\begin{array}{ccccc} x' & -1 & -\beta_p & \beta_p & x' \\ \frac{d}{dt} T' & = \frac{C^{ss}}{1-C^{ss}} & \frac{-1 + BC^{ss}}{1-C^{ss}} - \beta_p & \beta_p & T' \\ T'_c & 0 & \frac{1}{Le} & - \frac{(1 + \alpha_2)}{Le} & T'_c \end{array} \quad (3.1)$$

or

$$\frac{d}{dt} \vec{y}' = M \vec{y}'$$

with

$$\vec{y}' = [x', T', T'_c]^t$$

where  $x' = -BC' + T'$ , and  $M$  is the Jacobian matrix occurring in (3.1). The primed variables denote perturbations about the steady state, i.e.,  $T' = T - T^{ss}$ ,  $C' = C - C^{ss}$ ,  $T'_c = T_c - T_c^{ss}$ . If the perturbations grow

exponentially with time having a growth constant  $s$ , i.e.,

$x' = x^* e^{st}$ , we obtain

$$s \vec{y}^* = M \vec{y}^* \quad \text{where} \quad \vec{y}^* = [x^*, T^*, T_C^*]^t$$

The stability of the steady state is now determined by the three eigenvalues  $s$  of the matrix  $M$ . If all three eigenvalues have negative real parts, i.e., lie in the left half plane of the complex domain, the steady state is asymptotically stable. If one of the real eigenvalues turns from negative to positive as we vary a parameter, while the other two eigenvalues lie in the left half plane we have a steady-state bifurcation, i.e., the solution jumps from one stable steady state to another steady state. If, however, the real part of a complex conjugate pair of eigenvalues changes sign, i.e., goes from negative to positive, while the other eigenvalue remains negative, the steady state becomes unstable and we see the onset of oscillations or limit cycles. The dependent variables now vary periodically with time. Thus a study of the eigenvalues ' $s$ ' of  $M$  gives us information about the stability of the steady state and the nature of the onset of instability.

The eigenvalues  $s$  of  $M$  are given by the roots of the cubic characteristic equation

$$s^3 - Tr s^2 + P s - D = 0 \quad (3.2)$$

Here  $Tr$ ,  $P$ ,  $D$  represent the trace, sum of the principal (2x2) minors, and determinant of the matrix  $M$ . The expressions for  $Tr$ ,  $P$ ,  $D$  are

$$\text{Tr} = \frac{1}{(1-z)} \left[ -Bz^2 + z \left( B + 1 + \beta_p + \frac{(1 + \alpha_2)}{Le} \right) - \left( 2 + \beta_p + \frac{(1 + \alpha_2)}{Le} \right) \right] \quad (3.3)$$

$$P = \frac{1}{(1-z)} \left[ z^2 B \left( 1 + \frac{(1 + \alpha_2)}{Le} \right) - z \left( B + \frac{B(1 + \alpha_2) + \beta_p \alpha_2 + (1 + \alpha_2)}{Le} \right) + \left( \frac{2(1 + \alpha_2) + \beta_p \alpha_2}{Le} + 1 + \beta_p \right) \right] \quad (3.4)$$

$$D = \frac{(1 + \alpha_2)}{(1-z)Le} (-Bz^2 + Bz - (1 + \beta_M)) \quad (3.5)$$

Here the variable  $c^{ss}$  has been replaced by  $z$  for convenience. The expressions for  $\text{Tr}$ ,  $P$ ,  $D$  are all quadratic in  $z$ . The expression for  $D$  is exactly like Poore's determinant except we have  $\beta_M$  instead of  $\beta$ . The expression for  $\text{Tr}$  is identical with that of Poore's trace if we treat  $\beta_p + \frac{(1 + \alpha_2)}{Le}$  as  $\hat{\beta}$  (with  $\hat{\beta}$  playing the role of his  $\beta$ ). Note that in general  $\beta_p \neq \beta_M \neq \hat{\beta}$ . Conditions for steady state bifurcation and Hopf bifurcation will now be given.

The necessary and sufficient condition for asymptotic stability of the steady state is  $\text{Re}(s) < 0$  for all three roots of equation (3.2). In terms of the coefficients of the cubic this translates to (Porter, 1968),

$$\text{Tr} < 0, P > 0, D < 0, \text{Tr}P - D < 0$$

The characteristic cubic can have either all three real roots or one real root and a pair of complex-conjugate roots. This is decided by the discriminant of the cubic,  $\delta$ , where

$$\delta = 4P^3 - P^2\text{Tr}^2 + 27D^2 + 4D\text{Tr}^3 - 18\text{Tr}PD$$

For  $\delta < 0$  we have all three real roots and for  $\delta > 0$  we have one real root and a complex-conjugate pair, and  $\delta = 0$  corresponds to three real roots of which at least two are equal.

In terms of the cubic coefficients, the conditions for steady-state bifurcation is

$$D = 0, \text{Tr} < 0, P > 0. \quad (3.6)$$

For Hopf bifurcation the corresponding conditions are

$$\text{Tr}P - D = 0, \text{Tr} < 0, P > 0, \text{ and } \delta > 0. \quad (3.7)$$

Steady-state bifurcation. The condition for steady-state bifurcation  $D = 0$  can be obtained by solving the quadratic expression in (3.5). The quadratic is similar to Poore's expression with our  $\beta_M$  replacing his  $\beta$ . Thus for a fixed value of  $\beta_p$ ,  $\alpha_2$ ,  $B$ , we calculate the value of  $z$  and hence  $Da$  at which this bifurcation occurs. Note that this kind of instability is independent of  $Le$ . In order to observe this instability the conditions  $\text{Tr} < 0$ ,  $P > 0$  must also be satisfied. This ensures we have two eigenvalues with negative real parts and one real eigenvalue equal to zero.

The quadratic expression occurring in  $D$  is identified with the quadratic expression arising from the imposition of the monotonic variation of  $C^{SS}$  with  $Da$ . Thus once again for  $B \leq 4(1 + \beta_M)$  we have no

steady-state bifurcation. For  $B > 4(1 + \beta_M)$  the quadratic in  $D$  has two real roots. The points of steady-state bifurcation hence correspond to the turning points of the S-shaped curve of  $C^{ss}$  versus  $Da$  provided conditions (3.6) hold. The occurrence of multiple steady states gives rise to hysteresis and steady-state bifurcation. A sufficient condition for instability arising from the determinant is  $D > 0$ . This condition prevails in the middle branch of the S-shaped curve. Note that this condition is the opposite of the condition of the classical CSTR problem, where  $D < 0$  is sufficient for instability. The model hence has a very close parallel to Poore's model. The steady-state behavior does not give rise to any new phenomena.

Hopf bifurcation and the onset of limit cycles. The necessary and sufficient condition for Hopf bifurcation is  $\dot{D} < 0$ ,  $\text{Tr} < 0$ ,  $P > 0$ ,  $\delta > 0$  and  $\text{Tr}P-D = 0$ . The condition  $\delta > 0$  ensures we have a complex conjugate pair of eigenvalues, and  $\text{Tr}P-D = 0$  ensures their real part is zero. The other conditions ensure the remaining real eigenvalue is negative.

The condition  $\text{Tr}P-D = 0$  gives rise to the following quartic in  $z$

$$\begin{aligned}
 & -B(B + BC_1)z^4 + ((B + 1 + \beta_p + C_1)(B + BC_1) \\
 & + B(B + BC_1 + C_2 + C_1) - BC_1)z^3 - (B(2C_1 + 1 + \beta_p + C_2) \\
 & + (2 + \beta_p + C_1)(B + BC_1) + (B + 1 + \beta_p + C_1)(B + BC_1 + C_1 + C_2) \\
 & - 2BC_1)z^2 + ((B + 1 + \beta_p + C_1)(2C_1 + 1 + \beta_p + C_2) + (2 + \beta_p + C_1)
 \end{aligned}
 \tag{3.8}$$



$$(B + BC_1 + C_2 + C_1) - BC_1 - (1 + \beta_M)C_1)z - (2 + \beta_p + C_1)$$

$$(2C_1 + 1 + \beta_p + C_2) + (1 + \beta_M)C_1$$

where

$$C_1 = \frac{(1 + \alpha_2)}{Le} \text{ and } C_2 = \frac{\beta_p \alpha_2}{Le}.$$

This can be rewritten as a quadratic in  $1/Le$  as

$$\begin{aligned} & (z-1)(Bz^2 - (B + 1 + \beta_M)z + (2 + \beta_M))\left(\frac{1 + \alpha_2}{Le}\right)^2 + \\ & [(z-1)(Bz^2 - Bz + 1 + \beta_p) + (Bz^2 - (B + 1 + \beta_M)z \\ & + (2 + \beta_M))(-Bz^2 + (B + 1 + \beta_p)z - (2 + \beta_p)) - \\ & (-Bz^2 + Bz - (1 + \beta_M))(1-z)]\left(\frac{1 + \alpha_2}{Le}\right) + \\ & (-Bz^2 + (B + 1 + \beta_p)z - (2 + \beta_p))(Bz^2 - Bz + 1 + \beta_p) = 0 \end{aligned} \quad (3.9)$$

The calculation of the Hopf-bifurcation points using the quadratic (3.9) is mathematically convenient. It is made feasible because the steady state is independent of  $Le$ . This enables us to fix all other parameters in the problem to compute the critical values of  $Le$  at which we have the onset of instability. The volume of the cooling jacket  $V_c$  occurs only in  $Le$  and in no other dimensionless parameter. Thus  $Le$  can

be used as a control parameter to study the dynamics of the CSTR. Varying  $Le$  would be equivalent to changing the coolant residence time.

Ray and Hastings (1980) modelled the CSTR by considering the thermal capacitance and material capacitance of the reactor to be different from those of the reacting fluid. This more general model contains a similar parameter ' $Le$ ' in their energy balance. They find that their model has periodic solutions for sufficiently low values of  $Le$  their Lewis number. Their parameter  $Le$  is different from our definition of  $Le$ . It however arises because of considering an additional thermal capacitance. They exploit successfully the independence of the steady state of the  $Le$  number to 1) calculate critical values of  $Le$  for Hopf bifurcations and 2) study relaxation oscillations under the limit of  $Le \rightarrow 0$ .

The two limiting cases of interest are  $Le \rightarrow \infty$  and  $Le \rightarrow 0$ . These allow an easy comparison of our results with Poore's results. Under these asymptotic conditions we derive conditions for the Hopf-bifurcation points.

Case of  $Le \rightarrow \infty$ . Under these conditions we divide equation (2.3) by  $Le$ , to get  $\frac{dT_c}{dt} = 0$  or  $T_c = T_c(t=0)$ , a constant. Here the thermal inertia of the cooling jacket is sufficiently high and prevents the coolant temperature from rising significantly past its initial value. Thus equation (2.3) is decoupled from (2.2) and  $T_c$  can be regarded a constant  $T_c(t=0)$  in equation (2.2).

The Hopf bifurcation points can then be obtained for this case from the standard Poore model if we use our  $\beta_p$  for Poore's  $\beta$ . We obtain the same result by taking the limit  $Le \rightarrow \infty$  in the quartic to obtain the quadratic.

$$Bz^2 - (B + 1 + \beta_p)z + (2 + \beta_p) = 0$$

Case  $Le \rightarrow 0$ . Under this limit we make the pseudo-steady state approximation, i.e., we take equation (2.3) to be always at steady state. Under these conditions  $T_C$  becomes a fast variable (Mishchenko and Rozov, 1980). We eliminate  $T_C$  between (2.2) and (2.3). The dynamics of the reactor are then identical with those of the standard Poore reactor with his  $\beta$  now being replaced by  $\beta_M$ . Now the Hopf bifurcation points occur at the roots of the quadratic,

$$Bz^2 - (B + 1 + \beta_M)z + (2 + \beta_M) = 0$$

This is identical with Poore's Hopf bifurcation condition with  $\beta$  replaced by  $\beta_M$ . We thus see that under the two limits of  $Le \rightarrow 0$ ,  $Le \rightarrow \infty$  we recover the standard Poore problem for different values of  $\beta$ .

The effect of the finite thermal capacity ( $Le$ ) of the cooling jacket on the asymptotic stability of the steady states can be described using plots of  $Le_C$  versus  $Da$ . Here  $Le_C$  represents critical values of  $Le$ , i.e.,  $Le_C$  is the root of (3.9), when we fix  $z$ ,  $\alpha_2$ ,  $B$ ,  $\beta_p$ .

The quadratic (3.9) in  $Le$  can have a maximum of two positive real roots  $Le_{C1}$ ,  $Le_{C2}$  for some  $Da$ . Let  $Le_{C1} < Le_{C2}$ . For values of  $Le$ ,  $Le < Le_{C1}$ ,  $Le > Le_{C2}$  we have unstable steady states for those  $Da$ . For  $Le_{C1} < Le < Le_{C2}$ , we have asymptotically stable steady states for these  $Da$ . Instability under the conditions of  $Le \rightarrow 0$ ,  $Le \rightarrow \infty$  is to be expected since these asymptotic limits correspond to Poore's problem under the limit of  $\beta = \beta_M$ ,  $\beta = \beta_p$  respectively. We can verify these results from

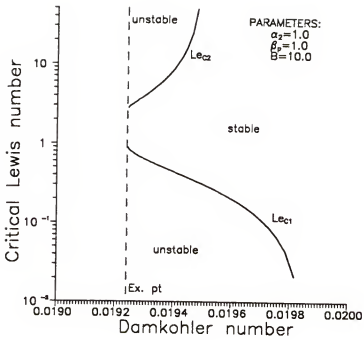


Figure 3.1. Critical Lewis numbers for stable and unstable states of conversion shown in Fig. 3.2

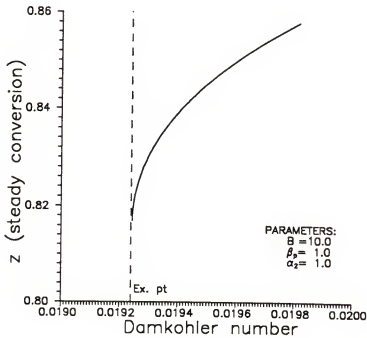


Figure 3.2. Steady state conversion

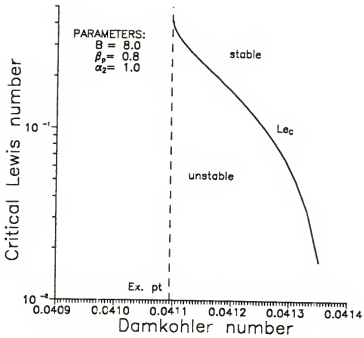


Figure 3.3. Critical Lewis numbers for stable and unstable states of conversion shown in Fig. 3.4

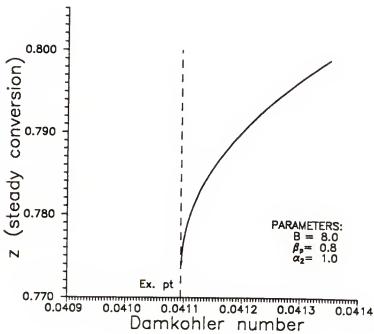


Figure 3.4. Steady state conversion

the stability of Poore's model for these values of  $\beta$ . Figure 3.2 depicts the steady-state conversion as a function of  $Da$  for a fixed  $B$ ,  $\beta_p$ ,  $\alpha_2$ . Figure 3.1 is the plot of the critical  $Le$  versus  $Da$  for the steady states shown in Fig. 3.2. The lower curve corresponds to  $Le_{C1}$ , the upper curve to  $Le_{C2}$ . For values of  $Da$ , where  $Le_{C1}$  exists the steady states are unstable for  $Le < Le_{C1}$ . If we design our reactor with  $Le > Le_{C2}$  the steady state is again unstable. Choosing  $Le$  such that  $Le_{C1} < Le < Le_{C2}$  for the  $Da$ ,  $B$ ,  $\beta_p$ ,  $\alpha_2$  shown assures us of an asymptotically stable steady state. Thus by appropriately choosing  $Le$  we can operate the reactor at an asymptotically stable steady state.

In Fig. 3.3 is a similar plot of  $Le_C$  versus  $Da$  for a fixed  $B$ ,  $\beta_p$ ,  $\alpha_2$ . The corresponding steady-state conversion is shown in Fig. 3.4. Here the combination of parameters is such that the equation (3.9) has only one positive real root  $Le_C$ . For  $Le > Le_C$  steady state for the corresponding  $Da$  shown in Fig. 3.4 is asymptotically stable. At  $Le < Le_C$  we have unstable steady states. Under such cases, we can operate at stable steady states by having sufficiently high values of  $Le$ . Ray and Hastings (1980) have a similar result. They find onset of limit cycles for sufficiently low values of their  $Le$ . Their definition of  $Le$  is quantitatively different from ours. It represents a measure of thermal inertia of the reactor and is hence similar physically.

## CHAPTER 4

### THE D-PARTITION METHOD AND APPLICATIONS TO THE CSTR MODEL

The first order exothermic reaction has been investigated by many researchers in great detail. Most publications (Poore (1973), Uppal et al. (1974, 1976)) to date have been concerned with the evaluation of the stability of a steady state for a fixed combination of parameter values. This approach to the problem, however, has some limitations. This problem is highly nonlinear and requires detailed calculations. Moreover, the resultant steady-state conversion of the reactor arises as a result of the problem and is not predetermined. In this section we wish to address the inverse problem, i.e.; what are the total possible combinations of parameter values which give us a desired level of conversion? Which of these parameter combinations yield an asymptotically stable fixed level of conversion?

In an industry it is usually of interest to run a reactor at a fixed level of conversion. It is hence necessary to see what combination of parameter values yield this particular conversion. We can then design our reactor appropriately. An elegant way of doing this is by using the D-partition method (Porter, 1968). We first describe the method, its salient features and its limitations. We conclude the chapter by applying it to a couple of situations.

The D-partition method can be used effectively to deal with characteristic equations whose coefficients depend on certain parameters  $\vec{p}$  ( $p_1, p_2, \dots, p_n$ ) linearly. Here  $p_1, p_2$ , etc. are scalars. The method

is used to divide the  $\vec{p}$  parameter space into different regions. It gives us information on how the roots of the characteristic equation change as we go from one region to another. In particular, we can identify the number of roots with negative real parts in each region. We then obtain the combination of parameter values where all roots of the characteristic equation have negative real parts indicating asymptotic stability. The application is particularly elegant to characteristic equations dependent on two parameters, as we can now depict graphically the different regions in a two dimensional diagram.

Let the characteristic equation be

$$F(s) = 0 \quad (4.1)$$

where  $F(s)$  is usually an  $n$ th order polynomial in  $s$ . Here  $s$  is a complex variable ( $\sigma + iw$ ). Over the complex domain the region of asymptotic stability is the left-half plane, the region where all roots have negative real parts. The D-partition method maps the boundary between the regions of stability and instability in the  $s$ -plane, i.e., the entire imaginary axis ( $s = iw$ ) into the parameter space of interest. This divides the entire parameter space into different regions. Each region can be denoted by  $D(k, n-k)$ ,  $0 \leq k \leq n$ , where  $k$  ( $n-k$ ) represents the number of roots of equation (4.1) with negative (positive) real parts, and  $n$  the order of polynomial. The region of asymptotic stability hence corresponds to the region  $D(n, 0)$ , where we have no roots with positive real parts. If we neglect the possibility of a characteristic root jumping from  $-\infty$  to  $+\infty$  an increase in number of roots with positive real parts can occur only as a result of a root crossing the imaginary axis



from the left to the right half plane. A root crossing the imaginary axis from the left to the right half plane as we vary parameters corresponds to a representative point in the parameter space moving from region  $D(k, n-k)$  to region  $D(k-1, n-k+1)$ . Thus for finite roots the  $D$  partition boundaries are the maps of the imaginary axis ( $s = iw$ ),  $-\infty < w < +\infty$  in parameter space.

This method is efficient and informative in constructing domains of stability in terms of parameters occurring in the problem. Although it is possible to construct these domains in more than two dimensional spaces it can be applied elegantly to problems containing one or two parameters. The method of construction of stability domains for the one and two parameter cases will now be demonstrated.

One parameter case. If the coefficient of the characteristic equation were to depend on one parameter, say  $\xi$ , linearly, we can rewrite equation 4.1 as

$$P(s) + \xi Q(s) = 0$$

or

$$\xi = - \frac{P(s)}{Q(s)} \quad (4.2)$$

The values of  $\xi$  corresponding to the imaginary axis in the  $s$ -plane is obtained by substituting  $s=iw$  in (4.2)

$$\xi(w) = - \frac{P(iw)}{Q(iw)} \quad -\infty < w < \infty \quad (4.3)$$

This equation now defines the D-partition boundary corresponding to finite roots. We let  $w$  vary from  $-\infty$  to  $+\infty$  and follow the locus traced by equation (4.3), in the  $\text{Re}(\xi)$  versus  $\text{Im}(\xi)$  plot. If we shade the left hand side of this locus as  $w$  increases from  $-\infty$ , then the shaded side corresponds to the more stable side of the boundary. Thus crossing a boundary from the shaded to the unshaded side corresponds to a root passing from the left to the right half of  $s$ -plane.

If all the boundaries are shaded according to the above convention, we can determine the value of  $k$  for each domain  $D(k, n-k)$  once we know the value of  $k$  for a domain. This is done by observing the number of times a boundary is crossed and decreasing or increasing the value of  $k$  according as the crossing is from the shaded to the unshaded side or vice versa. We thus obtain the region of asymptotic stability  $D(n, 0)$ . For a real parameter  $\xi$ , this asymptotically stable region reduces to the segments of the real axis in  $D(n, 0)$ .

The two parameter case. We now consider the case where the coefficients of the characteristic equation depend linearly on two parameters  $\xi, \eta$ . The equation (4.1) can now be rewritten as

$$F(s) = \xi P(s) + \eta Q(s) + R(s) = 0 \quad (4.4)$$

Taking

$$P(iw) = P_1(w) + iP_2(w)$$

$$Q(iw) = Q_1(w) + iQ_2(w)$$

$$R(iw) = R_1(w) + iR_2(w)$$

Along the imaginary axis ( $s=iw$ ), we obtain

$$F(iw) = \xi P_1(w) + \eta Q_1(w) + R_1(w) + i(\xi P_2(w) + \eta Q_2(w) + R_2(w)) = 0$$

This implies

$$\xi P_1(w) + \eta Q_1(w) + R_1(w) = 0 \quad (4.5)$$

$$\xi P_2(w) + \eta Q_2(w) + R_2(w) = 0$$

The D-partition boundaries corresponding to finite roots for

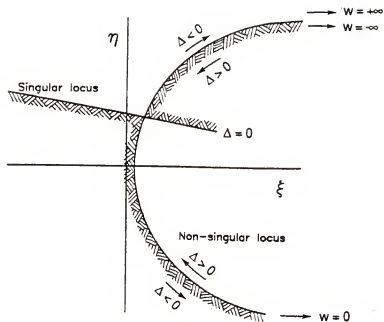
$$\Delta(w) = P_1 Q_2 - P_2 Q_1 \neq 0 \quad (4.6)$$

is

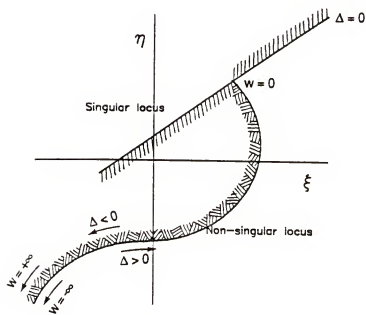
$$\xi = (-R_1 Q_2 + R_2 Q_1) / \Delta \quad (4.7)$$

$$\eta = (-R_2 P_1 + R_1 P_2) / \Delta.$$

For  $\Delta(w) \neq 0$  As  $w$  increases from  $-\infty$  to  $+\infty$  these equations trace out a locus in the  $\xi$ - $\eta$  plane which corresponds to a map of the imaginary axis in the  $s$ -plane. This is called the non-singular locus and is a part of the system of D-partition boundaries.



(a)



(b)

Figure 4.1. Shading rules for D-partition boundaries. Loci intersecting at (a)  $w \neq 0$ ; (b)  $w = 0$

If  $\Delta(w) = 0$  for some  $w$ , we obtain the corresponding singular locus by substituting the value of  $w$  in (4.5).

The various domains  $D(k, n-k)$   $0 \leq k \leq n$  must now be identified. To do this we need a convention to shade the various boundaries. If the axis in the  $\xi-\eta$  plane constitutes a right-handed orthogonal system, the non-singular locus must be shaded on the left for  $\Delta > 0$  and on the right for  $\Delta < 0$  if the locus is traversed in the direction of increasing  $w$ . It is usually found that the same curve is traversed twice, when  $w$  increases from  $-\infty$  to 0 and when  $w$  increases from 0 to  $\infty$  and  $\Delta$  reverses sign at  $w = 0, \pm \infty$ . Here the non-singular locus will be shaded twice on the same side. Crossing such a double shaded boundary corresponds to two characteristic roots crossing the imaginary axis simultaneously as we vary the parameters.

The rules for shading a singular locus depend on the value of  $w$  at which it intersects the non-singular locus (Porter, 1968). If the two loci intersect at a finite non-zero value of  $w$ , at which  $\Delta$  changes sign, the shading is done as in Fig. 4.1a. If the intersection occurs at a point on the non-singular locus at which  $\Delta$  changes sign, at  $w = 0, \pm \infty$ , the shading is done as shown in Fig. 4.1b. Here the shading is on the same side for both loci near the point of intersection, but beyond this point the shading passes to the other side of the singular line. If  $\Delta$  vanishes identically, the singular lines are the only boundaries.

Applications. In this section we discuss the application of the D-partition method to two chemical engineering problems.

(1) Classical CSTR. The classical CSTR system as modelled by Poore (1973) with a constant coolant temperature has a characteristic equation given by

$$F(s) = s^2 + (Bz^2 - (B+1+\beta)z + (2+\beta)) \frac{s}{(1-z)} + \frac{(Bz^2 - Bz + (1+\beta))}{(1-z)} = 0 \quad (4.8)$$

Here  $z$  represents conversion.  $B$  and  $\beta$  are the dimensionless parameters representing heat of reaction and heat transfer coefficient as defined by Poore. For a fixed  $z$  the steady state conversion level,  $F$  is now linear in  $B$  and  $\beta$ . Hence the method of D-partition can be applied to calculate stability domains elegantly in  $(B-\beta)$  space.

Using the method explained in the previous section, we find the singular locus corresponds to  $w=0$  and is

$$-Bz + \frac{\beta}{1-z} + \frac{1}{1-z} = 0. \quad (4.9)$$

The non-singular locus corresponds to

$$B(w) = \frac{w^2(1-z)^2 + 1}{z^2(1-z)}$$

$$\beta(w) = \frac{(1-z)(1 + w^2)}{z}.$$

Eliminating  $w^2$ , this reduces to

$$\beta = Bz + \frac{(z-2)}{(1-z)} \quad \text{for} \quad \beta > \beta_c = \frac{(1-z)}{z} \quad (4.10)$$

$$B > B_c = \frac{1}{z^2(1-z)}$$

The two locii intersect at  $\beta_c$ ,  $B_c$  and have been drawn in Fig. 4.2 for  $z = .5$  and shaded accordingly. The two locii (4.9, 4.10) are straight lines. The equation for the singular and non-singular locus is the same as the equation obtained by setting the determinant and trace of the Jacobian matrix to zero for a fixed  $z$ . They divide the  $B$ - $\beta$  parameter space into three regions A,B,C. Region A corresponds to  $B$ - $\beta$  combinations where the characteristic equation has two eigenvalues with negative real parts. In region B, one eigenvalue has a positive real part and the other a negative real part. In region C both characteristic roots have positive real parts. Thus  $B$ - $\beta$  values in region A give rise to a reactor which can operate at a fixed stable steady state conversion level of 50% if  $Da$  is chosen according to

$$Da = \frac{z}{1-z} e^{\frac{Bz}{1+\beta}}. \quad (4.11)$$

We have used the D-partition method to divide our parameter space into different regions. The method is elegant since the three dimensionless parameters  $Da$ ,  $B$ ,  $\beta$  in the problem can be determined explicitly for a fixed stable conversion level. The stability domain has been drawn in the  $B$ - $\beta$  parameter space. No nonlinear equations need to be solved in this method since we can use (4.11) to obtain  $Da$  explicitly for a fixed  $z$ ,  $B$ ,  $\beta$ . The design of a CSTR for a fixed conversion level can hence be done elegantly using this method.

Our ability to eliminate the steady-state temperature in favor of conversion using a linear transformation makes the method powerful. This enables us to fix the conversion of our reactor at the desired level. The temperature is now fixed automatically at a given level and

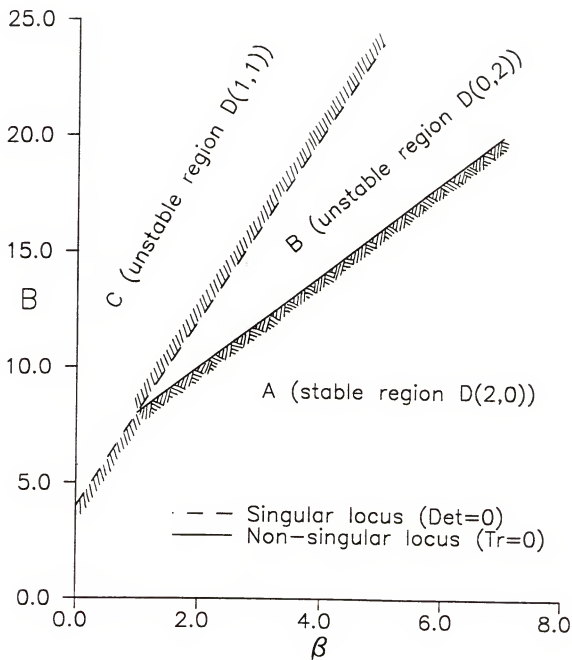


Figure 4.2. D-partition diagram for the classical CSTR, Poore model (1973)



we do not have to concern ourselves with it as long as it is not unrealistic. If we were unable to eliminate the steady-state temperature using our linear relationship, we would still be able to use the above method. The method, however, would only be locally valid for a certain fixed temperature and conversion. Our ability to eliminate temperature in favor of conversion makes our analysis globally valid.

(2) CSTR with coolant temperature non-constant. Here for our model equation (2.1-3) the characteristic equation (3.1) is a cubic.

$$s^3 - \text{Tr}s^2 + \text{Ps} - \text{D} = 0 \quad (4.12)$$

The coefficients  $\text{Tr}$ ,  $\text{P}$ ,  $\text{D}$  contain the parameters  $z$ ,  $\alpha_2$ ,  $\text{B}$ ,  $\beta_p$ ,  $\text{Le}$  (3.3-3.5). These parameters occur in nonlinear combinations with each other. It appears hence that the D-partition method is inapplicable. However, by fixing some of the parameters at fixed values, we can treat 4.12 to be linear in the remaining one or two parameters. This enables us to determine stability domains in terms of these parameters of interest.

In (4.12), by assigning values to  $z$ ,  $\alpha_2$ ,  $\text{Le}$ , we can treat the equation to be linear in  $\text{B}$ ,  $\beta_p$ . We can then evaluate stability domain in  $\text{B}-\beta$  space.

Fixing  $z$ ,  $\alpha_2$ ,  $\text{B}$ ,  $\beta_p$  enables us to treat the cubic equation as linear in  $1/\text{Le}$ . Stability domains in the  $\text{Re}(\frac{1}{\text{Le}})$  versus  $\text{Im}(\frac{1}{\text{Le}})$  plots can then be obtained. With a view to verifying the Figs. 3.1, 3.3 the D-partition diagrams for (4.12) were drawn in terms of  $1/\text{Le}$ . Figure 4.3 is the D-partition diagram which corresponds to Fig. 3.1. Here  $\text{B}$ ,

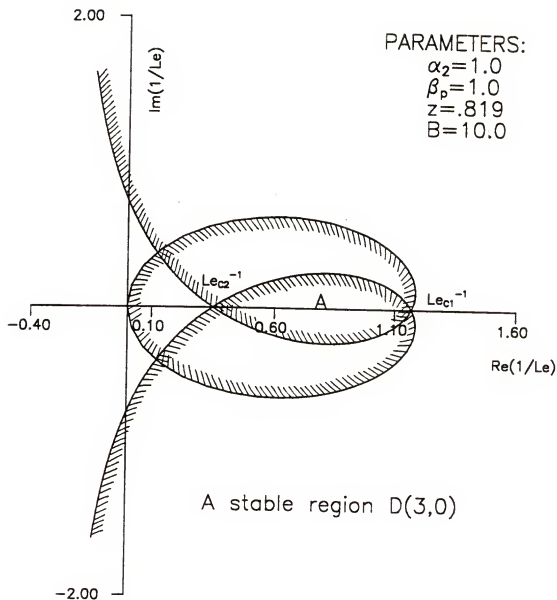


Figure 4.3. D-partition diagram in  $1/Le$  plane of equation (4.12)

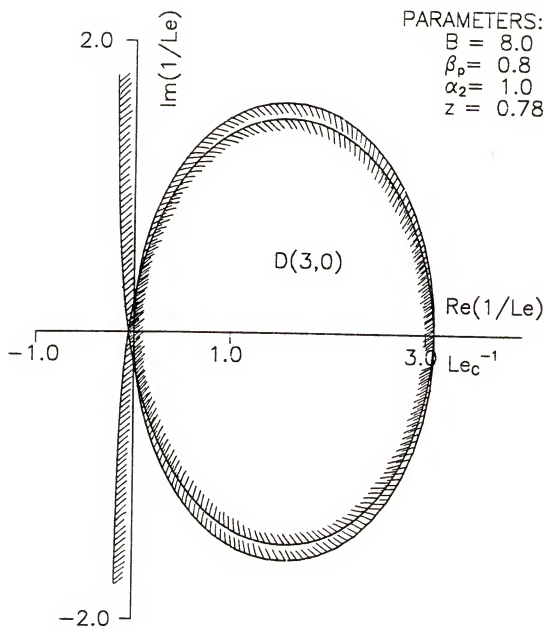


Figure 4.4. D-partition diagram in  $(1/\text{Le})$  plane of equation (4.12)

$\beta_p, \alpha_2$  have been fixed at the same values as in Fig. 3.1. We choose a  $z$  and hence a  $Da$  from Fig. 3.2, at which we have a  $Le_{C1}, Le_{C2}$  in Fig. 3.1 and obtain the corresponding region of stability  $A, D(3,0)$ . Since the parameter  $Le$  is real, the values of  $Le$  ensuring stability for the chosen steady state is the section of the real axis in  $D(3,0)$ . This is bounded on the real axis between  $Le_{C1}, Le_{C2}$ . Thus the region of stability is  $Le_{C1} < Le < Le_{C2}$  as found in Fig. 3.1.

For the D-partition diagram in Fig. 4.4 the parameters  $B, \beta_p, \alpha_2$  were chosen to be the same as those in Fig. 3.3. Choosing a  $z$  from Fig. 3.4, we find the corresponding region of stability as the intercept of  $D(3,0)$  on the real axis, i.e.,  $Le > Le_C$ . The other intercept of the boundary passes through the origin or  $Le = \infty$ . This confirms the result of Fig. 3.3.

The D-partition method can be used to design a cooling jacket for the stable operation of a reactor at a given steady state. This is possible since the parameter  $V_c$  occurs only in  $Le$  and in no other parameter.

## CHAPTER 5 CONCLUSIONS AND SCOPE

The use of different nonlinear models in chemical engineering is an old concept. In this dissertation the standard model for the CSTR has been modified and extended to a more realistic model by considering the finite thermal capacity of the cooling jacket. The D-partition method and its applications to the standard CSTR model and the model developed here have been studied. The different phenomena, like multiple steady states, limit cycles observed in Poore's model of the CSTR occur over a very narrow range of parameter values. It, hence, appears that these phenomena are more an exception than the rule, and the natural characteristic of the reactor is to have stable steady states. The finite thermal capacity of the cooling jacket was included in the model to see if the region in parameter space exhibiting limit cycles became wide or not. It appears that the region over which we see Hopf bifurcation does decrease and hence the finite thermal capacity has a stabilizing influence on the steady states.

The disappearance of the Hopf-bifurcation points for some values of  $Le$  raises the question--do we have an isola of periodic solutions? And if we do, are there any methods of predicting such isolas? Preliminary simulations of our equations show the presence of quasi-periodic solutions to our equations (2.1-2.3).

The parameter  $Le$  multiplies a time derivative term. Under the limits of  $Le \rightarrow 0$ ,  $Le \rightarrow \infty$ , we arrive at singular perturbation limits.

Under these limiting conditions, we have two vastly differing time scales. Some of the equations are always at steady state. Here some of the variables experience rapid, almost instantaneous, variations. The periodic solutions are discontinuous and now exhibit successive alternation between fast and slow motion. This kind of motion is called a relaxation oscillation. It would be important to study the dynamics of our system under different limits of parameter values to check for such oscillations. Such oscillations have been observed in many systems (Aluko and Chang, 1986).

In the second part of the dissertation, the D-partition method has been described. This method can be used to calculate stability domains in terms of the different parameters occurring in the model. Most models contain a large number of parameters. These usually occur in nonlinear combinations with each other. In the mathematical analysis of these models the effect of a parameter on the system dynamics is studied. The parameter is chosen usually from the point of view of mathematical convenience and is usually not a practical parameter which can be varied. In the D-partition method, we can study and choose a practically convenient parameter for the design of any system. This can be achieved by fixing the different parameters in the model at reasonable assigned values and constructing stability domains about the one or two parameters of interest which are chosen as control parameters.

Extension to flickering. There have been numerous studies on the onset of turbulence in natural convection (Howard and Krishnamurthy, 1986). These studies have focused on the different routes in the transition to turbulence. In natural convection, close to initiation the induced fluid motion is very regular. Under very high temperature

gradients the ordered fluid motion breaks down and gives rise to chaotic motion in the fluid phase. This chaotic motion induces a chaotic variation of the surface temperature. The phenomenon of "flickering" or random temperature fluctuations has been observed on catalytic wires or gauzes. It is possible that these are induced by natural convection. The initiation of natural convection induced by the exothermicity of a surface reaction has been studied by Viljoen and Hlavacek, 1987. We have to resort to complex numerical schemes to study the dynamics of these partial differential equations. The next step would be to retain the essential features of the model and simplify the mathematical equations to get a tractable system of equations.

At the initiation of natural convection cells are induced on the surface (Chandrasekhar, 1961). This induces a regular pattern of alternating hot spots and cold spots on the catalytic surfaces. These are in thermal communication with each other through the fluid and thermal conductivity of the catalyst. A simplified representation of this model would be a network of CSTRs each communicating with each other. This of course has also the advantage of being a lumped model. The first step towards studying such a network would now be to examine two CSTRs where the effluents from one is used as a coolant in the other and vice versa. This system has four dependent variables.

It has been known for a long time (Lorenz, 1963) that a system of three nonlinear ordinary differential equations although completely deterministic gives rise to chaotic motions. Since then there have been numerous models in a variety of disciplines exhibiting chaos. This has led people to believe that chaotic dynamics for a nonlinear system is more the rule than the exception. With a view to studying a system with

the minimum three dependent variables, the two CSTR networks described above can be further simplified. The coolant temperature can be used as a third state variable in the modelling of a single CSTR. The similarity between equations governing the CSTR and those modelling a surface reaction has been known for a long time (Aris, 1975). Under the limit of high thermal conductivity and low heat transfer coefficient, the equations become identical, as we can now neglect spatial variations and the two systems are described as lumped systems (see Appendix C). If we take into account the heat gained by the reactant fluid due to the exothermicity of the surface reaction, the modelling equations of the surface reaction become identical to equations (2.1-3). Thus any chaotic dynamics exhibited by our system can be possibly used to interpret the occurrence of flickering. It would thus be of interest to study the possibility of equations (2.1-3) exhibiting chaotic motions.



APPENDIX A  
DERIVATION OF THE GOVERNING LUMPED EQUATIONS OF A CSTR

In this appendix the governing dimensionless equations for the CSTR are derived. In general the coolant temperature varies along the cooling coil. The lumped energy balance for the coolant is derived rigorously using a formal perturbation argument. The reactor is assumed to be well mixed. We neglect spatial variations in the reactor.

The mass balance equation written for the reactor is

$$V \frac{dC_A}{dt} = q(C_{in} - C_A) - V k_A e^{-E/RT} \quad (A.1)$$

The energy balance equation written for the reactor is

$$V \rho C_p \frac{dT}{dt} = q \rho C_p (T_{in} - \tilde{T}) + (-\Delta H) V k_A e^{-E/RT} - UA(\tilde{T} - \tilde{T}_c) \quad (A.2)$$

We represent the cooling coil as a tubular reactor with no reaction occurring in it. The energy balance for the coil is then

$$\rho_c C_{p_c} \frac{\partial \tilde{T}_c}{\partial t} = k_T \frac{\partial^2 \tilde{T}_c}{\partial x^2} - v_c \frac{\partial \tilde{T}_c}{\partial x} + US(\tilde{T} - \tilde{T}_c)$$

subject to

$$\frac{\partial \tilde{T}_c}{\partial x}(0) = \epsilon(\tilde{T}_c(0) - T_{cin}) \quad \frac{\partial \tilde{T}_c}{\partial x}(1) = 0 \quad (A.3)$$

where

$$\epsilon = (v_c \rho_c C_{p_c} l) / k_T$$

All the variables are explained in the Notation. Here  $\tilde{T}_c$  varies with space and time. The space coordinate 'x' along which  $\tilde{T}_c$  varies is measured along the cooling coil. We seek the form of these equations under the limit  $\epsilon \rightarrow 0$  i.e. infinite thermal conductivity of the fluid. We expand the  $\tilde{T}_c$  in a formal perturbation series as

$$\tilde{T}_c = \sum_{i=0}^{\infty} \tilde{T}_{ci} \epsilon^i \quad (\text{A.4})$$

Substituting (A.4) into (A.3) and equating powers of  $\epsilon$ , we obtain

$$O(\epsilon^0) \quad \frac{\partial^2 \tilde{T}_{co}}{\partial x^2} = 0 \quad \text{with} \quad \frac{\partial \tilde{T}_{co}(0)}{\partial x} = 0 = \frac{\partial \tilde{T}_{co}(0)}{\partial x} \quad (\text{A.5})$$

This yields  $\tilde{T}_{co}$  is independent of x. Its variation with time is determined by

$$O(\epsilon^1) \quad \rho_c C_{p_c} \frac{\partial \tilde{T}_{co}}{\partial t} = \frac{\partial^2 \tilde{T}_{c1}}{\partial x^2} - US(\tilde{T} - \tilde{T}_{co}) \quad (\text{A.6})$$

$$\frac{\partial \tilde{T}_{c1}(0)}{\partial x} = \tilde{T}_{co}(0) - \tilde{T}_{cin}$$

$$\frac{\partial \tilde{T}_{c1}(1)}{\partial x} = 0$$

Integrating (A.6) with respect to  $x$  and using the boundary conditions and remembering  $\tilde{T}_{co}$  is independent of  $x$ , we arrive at

$$\rho_c C_{p_c} V_c \frac{d\tilde{T}_{co}}{dt} = (\tilde{T}_{cin} - \tilde{T}_{co}) - UA(\tilde{T} - \tilde{T}_{co}) \quad (A.7)$$

To a first order approximation, i.e., in the limit  $\epsilon \rightarrow 0$ , we can approximate the coolant jacket temperature as  $\tilde{T}_c(x, t) \approx \tilde{T}_{co}(t)$ .

Defining a dimensionless temperature  $T$  as  $T = \frac{E}{RT_{in}^2} (\tilde{T} - T_{in})$  we can rewrite

$$\begin{aligned} e^{-E/RT} &= e^{-E/RT_{in}} \frac{1 + T \left( \frac{RT_{in}}{E} \right)}{1 + T} \\ &\approx e^{-E/RT_{in}} e^T. \end{aligned}$$

This is the exponential approximation. It is accurate in the limit  $E \rightarrow \infty$ . Under this limit  $1 \ll T(RT_{in})/E$ . If we now define the dimensionless parameters  $B$ ,  $\beta_p$ ,  $\alpha_2$ ,  $Le$ ,  $Da$  as in the text, equations (A.1, A.2, A.7) reduce to equations (2.1-2.3).

# APPENDIX B VERIFICATION OF THE MODEL WITH EXPERIMENTS IN THE LITERATURE

There have been a few experimental studies on the onset of oscillations. Baccaro et al. (1970) studied the hydrolysis of acetyl chloride, Bush (1969) studied the vapor phase chlorination of methyl chloride and Vermeulen et al. (1986) studied the hydration of 2,3 epoxy-1 propanol catalyzed by sulfuric acid. In this appendix the experimental data presented in the above mentioned papers have been used to compute the dimensionless parameters occurring in our model. These values are presented in Table B1. The order of magnitude estimates for the various dimensionless parameters in Table 1 of the text are based on these values.

Table B1. Dimensionless parameters calculated from experimental data in literature

	Baccaro et al. (1970)	Bush (1969)	Vermeulen et al. (1986)
B	14.8	40.0	31.7
$\beta_p$	5.3	2.0	6.3
Da	.14	---	.02
Le	.06	---	---
$\alpha_2$	.77	---	---

The data of Baccaro et al. is complete as we know the values for all five parameters from their experiments. For the set of parameters of

Baccaro et al. our model predicts oscillations around a mean value of 17°C. They observe oscillations around 22°C.

APPENDIX C  
EQUIVALENCE OF THE EQUATIONS GOVERNING A CSTR AND  
THOSE OF A SURFACE REACTION ON A WIRE

In this appendix we establish the similarity between the equations modelling our CSTR and those modelling a surface reaction on a wire. For this we need to incorporate the heat gained by the reactant gas stream. This forces us to consider an energy balance for the reactant gas stream. Following Edwards et al. (1973), we write the dimensionless mass and energy balance equations as

$$\frac{dC_A^W}{dt} = 1 - C_A^W - Da^W C_A^W e^{T^W} \quad (C.1)$$

$$\frac{\partial T^W}{\partial t} = \frac{1}{\epsilon^W} \frac{\partial^2 T^W}{\partial x^2} + (T_g^W - T^W) + B^W Da^W C_A^W e^{T^W} \quad (C.2)$$

subject to

$$\frac{\partial T^W}{\partial x} + h(T^W - T_{gin}^W) = 0 \text{ at } x = 1$$

$$\frac{\partial T^W}{\partial x} - h(T^W - T_{gin}^W) = 0 \text{ at } x = 0$$

In the writing of these equations we have neglected diffusion of active sites and assumed the wire length is finite. The energy balance equation for the gas stream is

$$Le^w \frac{dT_g}{dt} = \alpha_2^w (T_{gin} - T_g) + (T^w - T_g) \quad (C.3)$$

The superscript  $w$  has been used to denote the variables and parameters for the reaction on a wire which are analogous to the CSTR. Here  $\epsilon^w$  is a parameter inversely proportional to the thermal conductivity of the wire. We seek the limiting form of these equations as  $\epsilon^w \rightarrow 0$ . The state variables are expanded in a power series of  $\epsilon^w$  as

$$T^w = \sum_{i=0}^{\infty} T_i^w (\epsilon^w)^i \quad (C.4)$$

Substituting (C.4) into (C.2) we obtain

$$\frac{dC_{Ao}^w}{dt} = 1 - C_{Ao}^w - Da^w C_{Ao}^w e^{T_o^w} \quad (C.5)$$

$$Le^w \frac{dT_{go}}{dt} = \alpha_2^w (T_{gin} - T_{go}) + (T_o^w - T_{go}) \quad (C.6)$$

$$\frac{\partial^2 T_o^w}{\partial x^2} = 0, \quad \frac{\partial T_o^w(0)}{\partial x} = \frac{\partial T_o^w(1)}{\partial x} = 0 \quad (C.7)$$

Equation C.7 yields  $T_o^w$  is independent of  $x$ , i.e., it is a constant throughout the wire. Its variation with time is found from the next order term

$$\frac{dT_o^w}{dt} = \frac{\partial^2 T_1^w}{\partial x^2} + (T_{go}^w - T_o^w) + B^w Da^w C_{Ao}^w e^{T_o^w} \quad (C.8)$$

$$\frac{\partial T_1^w}{\partial x} = h(T_o^w - T_{gin}^w) \text{ at } x = 0$$

$$\frac{\partial T_1^w}{\partial x} = -h(T_o^w - T_{gin}^w) \text{ at } x = 1$$

Integrating (C.8) over  $x$  we obtain

$$\frac{dT_o^w}{dt} = 2h(T_{gin} - T_o^w) + (T_{go} - T_o^w) + B^w Da^w C_{Ao}^w e^{T_o^w} \quad (C.9)$$

The analogy between equations (C.5, C.6, C.9) to equations (2.1-2.3) can be seen directly.



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## BIOGRAPHICAL SKETCH

Subramaniam Pushpavanam was born on October 1, 1961, in Madras, India. After his early education in Bombay, he went on to Calcutta in 1979 to finish his schooling. A sudden wave of interest in science at the end of his school days took him to the gates of the Indian Institute of Technology, Madras, where he earned his B. Tech. in chemical engineering in 1984. He joined the University of Florida in the fall of 1984 and obtained his M.S. in chemical engineering in 1985. He enrolled in the Ph.D. program immediately afterwards and has been a student since that time. He is planning on returning to India and working there.

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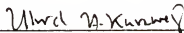
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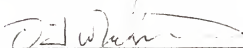
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